



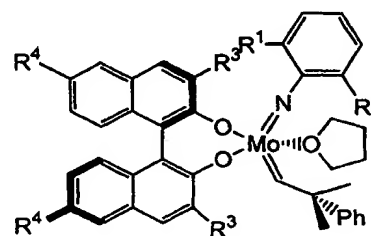
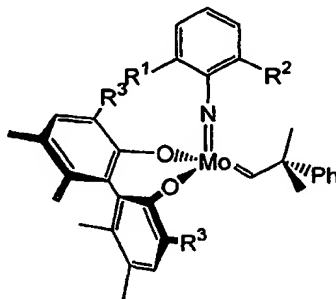
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(54) Title: ASYMMETRIC METATHESIS REACTIONS INVOLVING ACHIRAL AND MESO SUBSTRATES

(57) Abstract

A composition and method for the catalytic conversion of a racemic mixture of dienes to a cyclic olefin by a ring-closing metathesis (RCM) reaction are disclosed. The composition, a transition metal complex with an M=C reaction site, contains a bidentate dialkoxide of at least 80 % optical purity. Because the M=C reaction site is of a sufficient shape specificity, conferred in part by the dialkoxide of sufficient rigidity and a M=N-R¹ site, reacting the composition with a mixture of two enantiomeric dienes results in an olefin metathesis product that has at least a 50 % enantiomeric excess of one enantiomer in the mixture. A method is also provided for reacting a composition with a racemic diene mixture to generate a metathesis product that has an enantiomeric excess of at least 50 %. Methods are also provided for catalytic enantioselective desymmetrization. One method involves an olefin metathesis reaction with a molecular substrate having a plane of symmetry to form a product free of a plane of symmetry. Another method provides a desymmetrization reaction to occur in the absence of solvent. A method for producing quaternary carbon centers through a desymmetrization reaction is also described.

**1a:** R³ = *t*-Bu; R¹ = R² = *i*-Pr**1b:** R³ = *t*-Bu; R¹ = R² = Me**1c:** R³ = adamantyl; R¹ = R² = *i*-Pr**1d:** R³ = adamantyl; R¹ = R² = Me**1e:** R³ = ethyl; R¹ = R² = *i*-Pr**1f:** R³ = ethyl; R¹ = R² = Me**2a:** R³ = 2,4,6-tri(*i*-propyl)phenyl;R¹ = R² = *i*-Pr;**2b:** R³ = 2,4,6-tri(*i*-propyl)phenyl;R¹ = R² = Me**2c:** R³ = *t*-Bu; R¹ = R² = *i*-Pr;R⁴ = *t*-Bu**2d:** R³ = *t*-Bu; R¹ = R² = Me;R⁴ = *t*-Bu**2e:** R³ = Ph; R¹ = R² = *i*-Pr; R⁴ = H**2f:** R³ = Ph; R¹ = R² = Me; R⁴ = H